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(54) Title: ION EXCHANGE RESINS (57) Abstract A gold complex and/or silver complex selective ion exchange resin comprising a polyurethane matrix having an amine functionality and processes for recovery of gold and/or silver from solutions using the above ion exchange resin.		

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ION EXCHANGE RESINS

The present invention relates to a process for recovery
5 of gold and/or silver from solutions and ion exchange resins
for the recovery of gold and/or silver from solution.

The recovery of gold cyanide from solutions and from
pulp has been traditionally conducted using activated carbon
10 as a solid/liquid separation mechanism in what has become
known as the carbon-in-pulp (CIP) or carbon-in-leach (CIL)
process. Activated carbon in this recovery process however,
is known to suffer from a number of disadvantages including:

- 15 * poor resistance to attrition,
- * slower loading kinetics than ion exchange resins,
- * requires thermal regeneration for reactivation,
- * loads calcium and magnesium ions leading to pore
 blocking,
- 20 * sorbs organic materials from solution leading to
 lower gold cyanide recovery.

In plant pulps, contact is made by the activated carbon
with silica and alumina such that the carbon can become
25 saturated with fine slurry particles in less than three hours.
It has been reported that the equilibrium loading of fines was
independent of their concentration in the slurry. Furthermore,
the presence of these particles inside an adsorbent decreases
the effective diffusion of gold cyanide into the adsorbent
30 matrix.

Different batches of activated carbon even from the same
manufacturer have been found to have different properties. It
has been postulated that it is this difference which can
35 explain some of the differences in capacity and performance
which has been reported by different workers.

The problems associated with activated carbon have led

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workers in the field to evaluate and use ion exchange resins as an alternative solid/liquid separation material. It has been suggested that the advantages of a proposed resin-in-pulp (RIP) process may be:

5

(a) anion exchange resins are superior to currently available activated carbon with respect to both the kinetics of loading and the equilibrium loading of gold cyanide,

10

(b) resins may be eluted at room temperature, whereas activated carbon must be eluted at temperatures approaching 100°C,

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(c) activated carbon requires thermal reactivation,

(d) resins do not appear to be poisoned by organic species such as flotation reagents which have an adverse effect on carbon,

20

(e) resins do not load calcium carbonate to the same extent as activated carbon, and therefore do not require the same need for hydrochloric acid washing to remove precipitated calcite,

25

(f) minerals such as clays and shales can inhibit the performance of activated carbon. Resins do not suffer from this problem to the same extent,

30

(g) resins do not suffer from attrition to the same extent as activated carbon. Carbon losses are of the order of 25 to 40 g/tonne of ore treated, whereas resin losses are said to be approximately 5 to 10 g/tonne,

35

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(h) resins are not adversely affected by temperature increases to the same extent as is activated carbon during the adsorption stage,

5 (i) resins may be used to recover free cyanide ions or metal cyanide complexes from tailings streams.

10 Resins are not poisoned by organic species such as flotation reagents, machine oils and lubricants, solvents, etc. to the same extent as observed for activated carbon. It has also been observed that species such as hematite, shales, clays, alumina, etc. decrease the loading of gold on activated carbon and also act as "preg robbers"; the same decrease in loading is not reported for resins.

15

Known ion exchange resins are manufactured in bead form generally from polystyrene-divinyl benzene, acrylic, or phenol-formaldehyde resins. It has been proposed that ion exchange fibres can be produced from either polyacrylonitrile
20 onto which active ligands can be attached, or polypropylene fibres on to which polystyrene-divinyl benzene can be grafted. Ligands can then be attached to the surface of the ion exchange resins or fibres by conducting one or more suitable chemical reactions.

25

The performance of a number of commercial strong-base and weak-base ion exchange resins have been compared with activated carbons in actual plant solutions. The distribution coefficient of gold and the selectivity of gold over copper,
30 iron, cobalt, nickel and zinc provide a useful indicator of likely performance. The following conclusions may be drawn:

(a) Weak-base resins do not load aurocyanide to the same degree as strong-base resins, but are more
35 selective.

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- (b) Selectivity decreases with mixed functional group resins, being controlled by the ratio of quaternary ammonium groups to tertiary amine groups.
- 5 (c) Selectivity decreases as the degree of cross-linking increases.
- (d) Increasing the surface area to volume ratio, or porosity of the resin increases the loading.
- 10 (e) Generally, at a pH value of 10 or higher, weak-base resins only poorly load gold cyanide.
- (f) High concentrations of other metal cyanides efficiently compete with gold cyanide for loading sites on strong-base resins.
- 15 (g) Gold/copper selectivity varies with free cyanide ion concentration, (particularly with carbon), due to changes in $\text{Cu}(\text{CN})_2^- : \text{Cu}(\text{CN})_3^{2-}$ ratio.
- 20 (h) $\text{Zn}(\text{CN})_4^{2-}$ and $\text{Co}(\text{CN})_6^{3-}$ load strongly onto many ion exchange resins but not onto carbon.
- 25 (i) Background salts increase the gold loading onto carbon but can depress the loading onto weak-base (in particular) and strong-base resins.

Furthermore, it has been shown that whilst certain
30 macroporous resins provide good selectivity for gold cyanide, these same resins exhibited poor elution with 1% NaCN + 1% NaOH at 90°C. These particular resins were noted for their good resistance to attrition in pulps.

35 A problem associated with proposed RIP processes is one of resin loss. The following potential sources of resin loss in an RIP plant have been identified:

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- (a) abrasion of the resin beads by physical contact with the ore pulp,
- 5 (b) fracturing of the beads due to impact with moving mechanical parts during mixing, pumping, or screening of the resin and pulp,
- 10 (c) shattering of the beads due to osmotic shock caused by the cyclical swelling of the beads in an alkaline environment (loading) and contracting in an acidic environment (elution and regeneration).

To date, the resins evaluated for gold recovery have had several disadvantages, including, small particle size to
15 provide a large surface-to-volume ratio, lower selectivity for gold over other base-metal cyanides frequently present in leach liquors, and pK_a values which prevent the resin loading gold cyanide at pH values above 10.

20 Disadvantages of currently available ion exchange resins for gold recovery include:

- (a) purchase cost is higher than for activated carbon,
- 25 (b) the present need for fine sized beads (in order to achieve a significant concentration of ligands) renders it difficult to recover them from pulps by screening,
- 30 (c) stripping kinetics are slower and a more complex stripping regime is often required to effectively recover the gold cyanide for electrowinning.

In an attempt to address these identified sorption
35 selectivity and elution problems with presently available ion exchange resins a number of suggestions have been made.

Japanese Patent 78 06,296 suggests the use of

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guanidine-based ion exchange resins for the recovery and separation of gold from silver and platinum group metals.

UK Patent Application GB 2186563 A also suggests solvent
5 extractants and ion exchange resins based on the guanidine ligand.

South African Patent ZA 89/2733 and Canad. Patent
Application 2,005,259 also suggest the use of guanidine-based
10 resins.

None of these patents has addressed the additional problems of osmotic shock, particle size, or abrasion loss. PCT/AU93/00312, the disclosure of which is incorporated herein
15 by reference, relates to ion exchange resins comprising a polymer containing ion exchanging sites dispersed or distributed throughout a polyurethane matrix wherein the ion exchanging sites are introduced subsequent to the formation of the polyurethane matrix. It has surprisingly been found
20 that when the ion exchange resins of PCT/AU93/00312 are provided with an amine functionality that superior gold and/or silver extraction results are achieved. The particularly superior results as illustrated in the examples were not expected from a review of the prior art. The resins of the
25 present application are not restricted to the type described in PCT/AU93/00312 but include any polyurethane resin which has been provided with an amine functionality.

According to the present invention there is provided a
30 gold complex and/or silver complex selective ion exchange resin comprising a polyurethane matrix having an amine functionality.

The term "amine functionality" includes all nitrogen-
35 containing compounds including primary, secondary and tertiary amines, quaternary amine salts, aromatic or heterocyclic amines, guanidine-based complexes and imides.

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The polyurethane matrix may be a polyurethane foam or resin or an interpenetrated polyurethane foam or resin. A second polymer having the amine functionality may be dispersed or distributed throughout the polyurethane matrix or the
5 matrix may be provided with an amine functionality.

The term "dispersed or distributed" when used herein includes a dispersion of discrete particles as well as networks of polymers which are intimately mixed throughout or
10 incorporated within the polyurethane matrix such as in interpenetrating polymer systems.

The present invention also provides a process for the extraction of gold and/or silver from solutions including the
15 steps of:

- (a) contacting a gold complex and/or silver complex containing solution with the abovementioned resin;
- (b) separating the resin; and
- (c) recovering the sorbed gold complex by elution of
20 the gold complex from the resin.

The above resin and process are particularly useful to extract cyanide complexes from solution.

25 Polyurethane resins are noted for their abrasion and chemical resistance. These resins can be produced as beads, sheets or as fibres, but in particular, they may be expanded to form foams with the cellular properties varying from a microcellular expanded product to highly expanded foams with
30 a density of 10 kg/m³. By the correct selection of polyols, blowing agents and cell control agents these cells may be closed or open. In an open celled product, most of the cell windows are removed during production to leave only the struts behind. If a more open cellular product is desired, then the
35 polyurethane foam can be further improved by "reticulation", a mechanism well-known to those skilled in the production of polyurethane foams. Furthermore, if desired, particles including metal powders, metal alloy particles, inorganic

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materials (such as barytes), metal oxides (such as magnetite or ferrosilicon) may be added to the polyurethane to modify its final density and thereby match the density of the pulp solution and if required, to assist in recovery of the resin
5 from the aqueous solutions or pulps by magnetic means.

The ion exchange resin of the present invention comprises a urethane polymer as a matrix or continuous phase. Ways in which an amine functionality may be provided to the matrix are
10 described in PCT/AU93/00312 as follows. A second polymer may be dispersed or distributed throughout a polyurethane matrix, the second polymer being provided with an amine functionality. The amine functionality may be provided in a number of different ways. For example a polymer having no amine
15 functionality may be introduced into urethane raw materials, a polyurethane polymerisation reaction may then be conducted to form a polyurethane matrix having the polymer dispersed or distributed therein. The introduced polymer may then be chemically modified in one or more steps to provide the amine
20 functionality. In an alternative embodiment, a polyurethane resin may be interpenetrated with one or more monomers, at least one of which has one or more ligands attached. The one or more monomers may then be polymerised to provide a polymer containing said ligands. The ligands may either have an amine
25 functionality or be subsequently modified to provide an amine functionality. In yet another embodiment, a polyurethane matrix may be provided, the matrix may be interpenetrated with one or more monomers. The monomers may be polymerised to provide a polymer and the polymer may then be chemically
30 modified to provide an amine functionality.

As described above, polyurethane foams or resins can be interpenetrated with a second polymer prior to, during, or subsequent to production. Such an interpenetration may be by
35 any suitable polymer such as those described in PCT/AU93/00312. The dispersed or distributed phase polymer typically may be a polymer formed from monomers of styrene, acrylonitrile, vinyl chloride, vinylidene chloride, divinyl

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benzene, butadiene, epichlorohydrin, caprolactone, thiodiglycol, thiodianiline, diallylamine, methylacrylonitrile, hydrazides, dicyclopentadiene, vinyl butyral, succinic anhydride, allyl halides, allyl malonic acid, acryloyl chloride, polyacetal, vinyl alcohol, aminosalicyclic acid, dimethylolpropionic acid, α -methyl styrene, p-methyl styrene, acrylates such as methylmethacrylate, acrylamide, methylacrylamide, acrylic acid, hydroxyethyl acrylate, hydroxypropyl acrylate, glycidyl methacrylate, ethylene dimethacrylate, methylacrylic acid, hydroxyethyl methacrylate, ethylene glycol dimethacrylate, ethyl acrylate, acrylimido salicylic acid, acrylimido diacetic acid, acrylimido malonic acid, acrylimido phthalic acid, acrylimido glycolic acid, N,N'-methylenebisacrylamide, 1-vinylimidazole, vinylpyridine, styrylguanidine complexes, diallyldimethylammonium chloride, styryl imidazoline complexes, or combinations of these monomers or chemical modifications of these monomers but is not limited to these monomers. Such chemical modification may be, for example, chlorination, chloromethylation, hydroxylation, nitration, amination and the like. Examples are styrene monomer reacted with divinylbenzene, subsequently chloromethylated and then aminated; chloromethylstyrene polymerised and then aminated; acrylonitrile monomer polymerised and then aminated; 1-vinylimidazole copolymerised with methylbisacrylamide; acrylonitrile polymerised with styrene monomer or divinylbenzene and then aminated.

Typical polymers which may form the dispersed phase include polystyrene, styrene-divinyl benzene, styrene-acrylonitrile, styrene-acrylonitrile-methylmethacrylate, acrylonitrile-methylmethacrylate, polyacrylonitrile, polyacrylates, acrylic or methacrylic esters, acrylonitrile-unsaturated dicarboxylic acid-styrene, vinylidene chloride-acrylonitrile, epoxy(glycidyl methacrylate)-acrylonitrile, poly p-methylstyrene, polyureas, aniline-phenol-formaldehyde, phenol-formaldehyde, styrene-butadiene, styrene-acrylonitrile-butadiene, acrylonitrile-polyethylene glycol, polyamides,

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polyacrylamides, polyimidazoles, allylglycidyl ether adducts of diamines, ethylene and propylene carbonate adducts of diamines, polybutadiene-acrylates, polydiallylamine, epoxy adducts, polycaprolactone, caprolactone-acrylates, 5 polydicyclopentadiene, styrene-methacrylonitrile, methacrylonitrile-divinylbenzene, polyvinyl chloride, glycidyl methacrylate-ethylene dimethacrylate, acrylonitrile-methylacrylic acid, polyvinyl alcohol-acrylonitrile, methyl methacrylate-hydroxyethyl acrylate, hydroxyethyl methacrylate-10 oligo(ethylene glycol)dimethacrylate, hydroxystyrene-methylmethacrylate, polyethyl acrylate-polystyrene, crosslinked butadiene, polystyrene-polyethyleneimine, polystyrene-arsenazo, epoxy-polystyrene, epoxy-diaza crown ethers, polyacetal, cresol sulphonic acid-phenol-formaldehyde, 15 anthraquinone-formaldehyde, acryloyl chloride-iminodiacetic acid, acryloyl chloride-aminosalicylic acid, acryloyl chloride-methyl nitrophenol-triethylamine, methyl nitrophenol-acetic anhydride-acrylic acid, hydroxy acetophenone-substituted benzoic acid-formaldehyde, or, other like polymers 20 or combination of polymers. Particularly suitable in the context of the present invention have been found to be polymers formed from a polystyrene-divinyl benzene, polyacrylonitrile and polyacrylates. The polymers may then undergo a further chemical reaction such as chloromethylation 25 or amination.

This second polymer may then be further reacted by suitable chemical modifications to include ligands. Examples of ways in which ligands can be introduced into a polyurethane 30 matrix are discussed in PCT/AU93/00312 but are by no means limiting. For example, by chloromethylation, chlorination, carboxylation, amination, phosphorylation, thioureation, diazotisation, amidoximation, oximation, etc. or other processes to attach specific ligands to the second polymer. 35 Preferred in the context of the present invention is chloromethylation. The chemical modification may also modify the polyurethane matrix. For example ligands may be attached to the amide groups, hydroxyl groups, reactive methyl groups,

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or to the aromatic ring of the isocyanate component of the polyurethane matrix if an aromatic isocyanate is used in the production of the polyurethane resin. Additionally, reactive sites may be incorporated into the polyurethane by modifying
5 an isocyanate with a material containing reactive sites (such as a dihydroxy compound) to form a prepolymer and further reacting the prepolymer with additional materials to produce the desired polyurethane. The polyurethane resin containing ligands such as chloromethylated sites may then undergo a
10 further chemical modification such as amination.

In a preferred embodiment, chloromethylstyrene may be substituted for polystyrene and therefore, an interpenetrated polyurethane resin containing chloromethylated polystyrene,
15 crosslinked with divinyl benzene or other suitable monomer may be produced. This resin may then undergo further chemical modification such as amination.

In a preferred embodiment of the invention the monomer(s)
20 or blend of monomer(s) and comonomer(s) is interpenetrated into a polyurethane matrix which has been provided with unsaturated sites during its manufacture. For example monomers, particularly reactive monomers, such as hydroxy ethyl methacrylate, octene diol, hexene 1,2 diol,
25 polybutadiene diol may be incorporated into the polyurethane during its manufacture to provide reactive unsaturated sites in the cured polyurethane. One or more different unsaturated monomers may then be interpenetrated into the cured polyurethane and polymerised. The resultant polymer is thus
30 chemically bound into the polyurethane matrix. Vinylpyridine, 1-vinylimidazole, diallyldimethylammonium chloride, [3-(methacryloylamino)propyl]trimethylammonium chloride, styryl guanidine and/or its complexes, styrylimidazole and/or its complexes, are examples of such monomers containing an
35 unsaturated functional group. Whilst it is preferred that the monomer(s) or blend of monomer(s) and comonomer(s) be interpenetrated into a polyurethane matrix containing an unsaturated group it is not a requirement of the invention

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that such reactive sites should be present in the polyurethane matrix.

Alternatively, a hydroxyl-containing compound may be
5 reacted with a diisocyanate to produce an isocyanate-terminated prepolymer. This prepolymer may then be included as one of the raw materials in the polyurethane resin manufacture. Examples of the reactive compound are octene diol, hexene 1,2 diol, polybutadiene diol. Examples of the
10 diisocyanate include toluene diisocyanate (TDI) and various grades of diphenylmethane-4,4'-diisocyanate (MDI). Prepolymer manufacturing techniques are well known to those skilled in the production of polyurethane resins.

15 An interpenetrated polyurethane which contains a suitable ligand may be induced to undergo a further chemical reaction such as alkylation. For example, a polyurethane may be interpenetrated with a second polymer such as vinylpyridine and then the pyridine site may be methylated by reaction with
20 a methyl halide or ethylated by reaction with an ethyl halide. The interpenetration may be conducted in the presence of a comonomer such as divinylbenzene. In a further example, a polyurethane resin containing an acrylonitrile polymer was reacted with an amine to form an imidazoline functional group
25 and then further reacted with a methyl or ethyl halide.

In another embodiment copolymer polyols may be produced by the grafting polymerisation of unsaturated monomers on to poly(ethylene oxide) (EO) or poly(propylene oxide) (PO) or
30 mixed EO-PO containing polyols. Typical monomers include styrene, divinylbenzene, acrylonitrile, acrylates, vinyl acetate, styryl guanidines, styryl imidazoles, vinylpyridine, 1-vinylimidazole and [3-(methacryloylamino)propyl]-trimethylammonium chloride and mixtures thereof. This polymer
35 polyol may then be incorporated as a raw material in the manufacture of a polyurethane. It is also possible for specific polymers to be induced to undergo further chemical reactions.

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Alternatively, a selected diisocyanate or isocyanate-terminated prepolymer may be reacted with amide groups or hydroxyl groups present in a polyurethane polymer. Suitable isocyanate monomers include toluene diisocyanate (TDI), PAPI (a polyaryl polymethylenepolyisocyanate as defined in U.S. Patent No. 2,683,730), triphenylmethane-4,4',4''-triisocyanate, benzene-1,3,5-triisocyanate, toluene-2,4,6-triisocyanate, diphenyl-2,4,4'-triisocyanate, xylene diisocyanate, chlorophenylene diisocyanate, various grades of diphenylmethane-4,4'-diisocyanate (MDI) and including mixtures containing adducts, dimers, trimers and higher functional isocyanates and/or carbodiimides and trifunctional cycloadducts, naphthylene-1,5-diisocyanate, xylene-alpha,3,3'-dimethyl-4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 4,4'-methylene(phenylisocyanate), 4,4'-sulphonylbis(phenylisocyanate), 4,4'-methylene diorthotolylisocyanate, ethylene diisocyanate, hexamethylene diisocyanate (HDI), methylene bis(cyclohexyl isocyanate), trimethylenediisocyanate, isophorone diisocyanate, 2,2,4-trimethyl-1,6-hexane diisocyanate, etc. Desired ligands can then be reacted with the unreacted isocyanate groups. For example, TDI, MDI or HDI may be reacted at elevated temperature in the presence of a urethane reaction catalyst such as triethylamine with hydroxyl groups and/or amide groups present in the polyurethane resin such that one of the isocyanate groups remains unreacted. This unreacted isocyanate group may then undergo a further reaction such as by amination by alkyl amines. Alternatively, the unreacted isocyanate group may then be reacted with water to form an amine. This amine site may then be induced to undergo a further chemical reaction if so desired.

Any suitable amine functionality may be introduced into the resin of the invention. As noted above the term "amine functionality" includes all nitrogen containing compounds including primary, secondary and tertiary amines, quaternary amine salts, aromatic or heterocyclic amines, guanidine-based complexes and imides. Preferred amination includes alkyl

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amines wherein the alkyl chain is preferably between 1 and 6 carbons long, or which can be reacted to form an imidazoline ligand, or guanidine, pyridine, quinoline, pyrrolidine, diallylamine, dibenzylamine, or other suitable amine as are more fully discussed below.

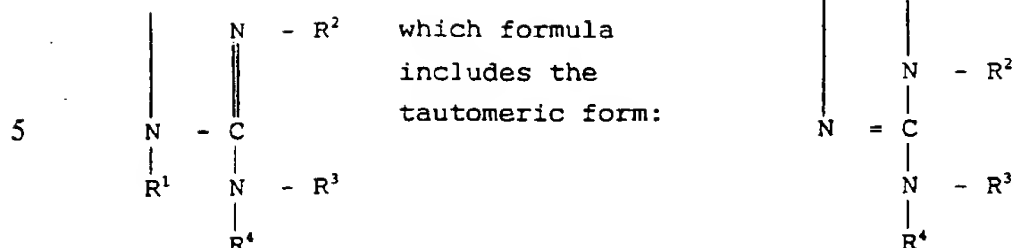
In a preferred embodiment of the present invention polyurethane foams incorporate polystyrene-divinyl benzene. The benzene ring is preferably then chloromethylated. Following this reaction, a further reaction may desirably be conducted in which amine functional groups are incorporated into the polyurethane foam or resin. Varying lengths of alkyl chain have been incorporated. Dimethylamine, diethylamine, diethanolamine, hexamethylenetetramine, ethylenediamine, 2-ethyleneiminoimidazoline, trimethylamine, triethylamine, tributylamine, dimethylethanolamine, are typical of such alkylamines.

In a similar manner, various guanidine functional groups have also been introduced into the polyurethane foam or resin. For example, guanidine, 2-ethylhexylguanidine, di-o-tolyl guanidine, di-n-alkyl guanidine, dioctylguanidine, N-(6-aminohexyl)-N'-butyl guanidine complexes, styrylimidazoline complexes, are examples of such ligands.

Other amine functionality introduced includes pyridine, quinoline, benzylamine, dibenzylamine, pyrrolidine, diallylamine, aminodiacetate, amino phosphonic acids, benzyldimethylamine, benzylimidazoline, 2-methylimidazoline (lysidine), benzyllysidine.

Other organic amines may also be incorporated into the polyurethane foam or polyurethane resin. This includes for example guanidine complexes or compounds having guanidine functional groups such as those disclosed in South African Patent ZA 89/2733 and having the formula:-

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in which each of R¹, R², R³, and R⁴ independently of each other, represent hydrogen, alkyl, alkenyl or aryl (including substituted aryl) with the further possibility that the functional group may be protonated and have a counter ion associated therewith;

and British Patent Application GB 2186563A containing the functional group:-



wherein R₁ through R₅ is selected from the group consisting of H, a resin, aromatic and aliphatic groups containing from 2-25 carbon atoms.

The contents of ZA 89/2733 and GB 2186563A are herein incorporated by reference and the term "guanidine complexes" when used herein includes those compounds disclosed in ZA 89/2733 and GB 2186563A.

In a further preferred embodiment, polyacrylonitrile or polyacrylonitrile copolymers such as with styrene or styrenedivinylbenzene is incorporated into the polyurethane foam. Amine functionality is then preferably introduced into the polymer. For example, diethylenetriamine and ethylenediamine have been reacted with the nitrile group introduced into the polyurethane resin. By the selection of reaction conditions, so imidazoline groups may be formed.

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Organic extractants including tributylphosphate, dibutyl butyl phosphate, trioctylamine, tri-(C₈-C₁₀) alkyl methyl ammonium chloride, guanidine functionality, imidazoline functionality such as lauroylimidazoline, may also be included
5 into the polyurethane foam or polyurethane resin.

The above description describes various ways of including an amine functionality on a polyurethane resin. It should be appreciated that more than one method may be used in
10 combination to include different types of amines and onto different parts of the ion exchange resin such as a first amine functionality on a second interpenetrated polymer and a second amine functionality grafted onto EO-PO polyol.

15 The resins of the present invention are also capable of impregnation with organic extractants which are capable of removing desired metal ions from solution. Any suitable amine extractant may be incorporated into the resin of the invention. Such amine extractants include trioctylamine,
20 guanidine functionality, tri-(C₈-C₁₀) alkyl methyl ammonium chloride, or other extractant, including tributylphosphate and dibutyl butyl phosphate. An example of such an extractant is Aliquat 336^(TM) [tri-(C₈-C₁₀) alkyl methyl ammonium chloride] a quaternary-based organic extractant manufactured by Henkel
25 Corporation. The incorporation of these extractants can be modified by either pre- or post-incorporation of a diisocyanate or a diisocyanate prepolymer onto the polyurethane foam and curing it such as by passing steam through the isocyanate-impregnated polyurethane foam
30 containing the organic extractant. Alternatively, the organic extractant may be blended with the diisocyanate component (providing that the organic reactant does not react with the diisocyanate to form a solid product prior to its incorporation onto the polyurethane foam or resin). Resins
35 of the invention may include an amine functionality and also contain an organic extractant.

The resins of the present invention offer exceptional

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abrasion resistance, and resistance to osmotic shock. These resins can be formed into particles of a size such that they can be readily recovered from gold and/or silver circuits. This particle size may be significantly larger than for
5 conventional ion exchange resins. As previously noted, conventional ion exchange resins require a small particle size to enable them to have sufficient exchange capacity. Conventional resins are also generally made macroreticular to increase their capacity and has been reported leads to osmotic
10 shock which can degrade the resin. It has been reported that this process may lead to pores being generated in the ion exchange resin which can block and reduce its capacity to remove metal ions from solution.

15 The resins of the present invention are particularly suitable for the extraction of gold and/or silver complexes, for example cyanide complexes from solutions. They may be used to extract gold cyanide from a gold cyanide containing solution which is part of a pulp or slurry.

20 It should be noted that the application of the polyurethane foams of the invention is not restricted to the recovery of gold cyanide only. Extraction of other gold complexes such as the gold halides, particularly chloride and
25 bromide, gold thiourea, gold thiosulphate, gold thiocyanate can also be achieved by the application of interpenetrated and modified polyurethane foams or impregnated polyurethane foams.

Silver cyanide and other silver complexes, particularly
30 thiosulphates, which may occur in solution, or in the recovery of silver from silver ores, or silver which may occur in association with gold in gold ores may also be recovered by the process of the invention.

35 Resins which are selective for different precious metals such as gold, silver and the platinum group metals may be produced and used to separate mixtures of precious metals.

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The solutions may be clarified, such as is normally obtained in gold heap leaching operations. Or it may be from pulps, such as occur in carbon-in-pulp or carbon-in-leach processes.

5

Stripping of the polyurethane resin of the invention may be accomplished by a suitable solvent such as sodium or ammonium thiosulphate, acidified thiourea, zinc cyanide, or in some instances, pH control by stripping at a pH in excess
10 of 12.

It has been proposed that chlorine, or hypochlorite, or bromine be used as lixiviants for gold. Activated carbon has been proposed for the recovery of gold chloride (CICL
15 process). Ion exchange resins have also been proposed for the recovery of these halides. The activated carbon rapidly reduces the gold to metallic gold by what is believed to be a diffusion-controlled mechanism. Therefore, the metallic gold will build up on the edges of the carbon and can easily be
20 abraded from its surface. Ion exchange resins have also been shown to reduce the gold to gold metal. In addition such resins may be oxidised by hypochlorite solutions.

A further advantage of the present invention is that
25 polyurethane foams do not suffer from hypochlorite degradation and will not reduce the gold to gold metal during the period that they are in the plant providing the solution conditions are correctly established. If reduction occurs, it is within the polymer, and therefore is not lost by abrasion as is the
30 case with activated carbon.

EXAMPLE 1

Polyurethane foams were interpenetrated with a mixture
35 of styrene monomer, divinyl benzene, and 2,2'-azobisisobutyronitrile (AIBN). The interpenetration and curing was conducted at 70°C in a nitrogen atmosphere. This foam was then chloromethylated by reacting 1 gram of the



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interpenetrated polyurethane foam at room temperature for 2 hours with 5 grams of octyl chloromethyl ether together with stannic tetrachloride catalyst in a suitable solvent.

- 5 This chloromethylated polyurethane foam was then further reacted with the amines as listed in Table 1 and under the conditions as given.

10 0.1 g of each of these aminated polyurethane foams were then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 10.5. Typical extraction results are given in Table 1. Capacity loadings included dimethylamine modification of 15,000 g Au/tonne polymer and 59,000 g Au/tonne of polymer for the pyridine modified
15 polyurethane. The excellent extraction properties of the polyurethane foam is shown by comparison with the details provided by Green et al. in their Canadian Patent Application 2,005,259 who indicated that a pyridine based polystyrene-divinyl benzene (9% DVB) extracted 23,400 g Au/tonne PS-DVB
20 from a synthetic pregnant solution.

TABLE 1 - Gold Cyanide Loading on Polyurethane Foams
Bearing Various Amine Functionalities

	Amino Ligand used	Reaction Conditions	Gold Loading, mg Au/kg resin
5	Dimethyl amine $(CH_3)_2NH$	40% aqueous solution - methanol, 40°C, 18h	> 10,000
	Trimethyl amine $(CH_3)_3N$	30% aqueous solution - methanol, 40°C, 24h	9,400
	Pyridine 	acetone, ref. 24h	> 10,000
10	Quinoline 	Toluene, 70-80°C, 24h	> 10,000
		acetone, reflux 24h	8,000
	TOA	toluene, 70-80°C, 24h	> 10,000
15	Guanidine $H_2N-C-NH_2$ NH	methanol, reflux, 24h	> 10,000
20	di-n-alkyl guanidine $R-NH-C-NH-R$ NH R=octyl, 2-ethyl hexyl etc.		9920

EXAMPLE 2

2.9 grams of a polyurethane foam in which 10 % by weight of polybutadiene diol was included as a raw material during its manufacture was interpenetrated with a mixture of 6 grams of acrylonitrile, 0.15 grams of divinyl benzene and 50 milligrams of AIBN as a polymerisation catalyst and then cured for 24 hours at 60°C in a nitrogen atmosphere. 1.0 grams of the resultant resin was then further reacted with 0.3 millilitres of diethylene triamine in toluene and in the presence of 20 milligrams of rubeanic acid as a catalyst at 70 to 80°C for 6 hours.

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 10.5. The polymer loaded 6,800 mg Au/kg of resin from solution. 53% of the gold cyanide was able to be stripped from the resin at room temperature in 18 hours by a 1M solution of sodium hydroxide.

EXAMPLE 3

3.8 grams of a polyurethane foam in which 10 % by weight of polybutadiene diol was included as a raw material during its manufacture was interpenetrated with a mixture of 10.1 grams of chloromethyl styrene monomer (CMS), 0.25 grams of divinylbenzene and 0.037 grams of AIBN and then cured at 70°C for 24 hours in a nitrogen atmosphere.

The resultant interpenetrated resin was then further reacted under the stated conditions with various amines as given in Table 2.

0.1 g of each of these aminated polyurethane foams were then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. Typical extraction results are given in Table 2.

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TABLE 2

Amine	Reaction Conditions	Gold Loading, mg Au/kg resin at pH=11
Pyridine	55°C in acetone, 24 hour	> 10,000
Dimethylamine	60°C in acetone, 18 hour	6,300
Guanidine	Stoichiometric quantity in water-methanol, 60°C, 24 hour	9,100
Dioctyl guanidine	Stoichiometric quantity in water-methanol, 60°C, 24 hour	> 9,800
Diethylene-triamine	70 to 80°C in toluene 18 hour	6,500

10

0.1 g of polyurethane foam containing the pyridine ligand was pulsed for 3 hours in 100 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 65,100 mg Au/kg of resin from solution.

15

0.1 g of polyurethane foam containing the dioctyl guanidine ligand was pulsed for 3 hours in 50 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 29,000 mg Au/kg of resin from solution.

20

EXAMPLE 4

1.5 grams of a polyurethane foam in which 10 % by weight of polybutadiene diol was included as a raw material during

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its manufacture was interpenetrated with a mixture of solvent, 4 millilitres of vinylpyridine, 0.25 grams of divinyl benzene and 20 milligrams of AIBN and then cured at 70°C for 24 hours under a nitrogen atmosphere.

5

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 6,900 mg Au/kg of resin from solution.

10

The resin from the Example was then methylated by reacting this resin with a 2 mole excess of methyl halide dispersed in a suitable solvent for 16 hours at room temperature.

15

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 9,700 mg Au/kg of resin from solution.

20

EXAMPLE 5

1.5 grams of a polyurethane foam in which 10 % by weight of polybutadiene diol was included as a raw material during its manufacture was interpenetrated with a mixture of 4 grams of methyl methacrylate monomer, 0.1 gram of divinylbenzene and 18 milligrams of AIBN and then cured for 24 hours at 70°C under a nitrogen atmosphere.

30

0.5 grams of this resin was then reacted with 0.5 grams of diethylene triamine in the presence of 20 milligrams of rubeanic acid as a catalyst at 70 to 80°C for 6 hours.

35

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 3,000 mg Au/kg of resin from solution.

EXAMPLE 6

1.5 grams of a polyurethane foam in which 10 % by weight of polybutadiene diol was included as a raw material during its manufacture was interpenetrated with a mixture of 4 grams of 1-vinylimidazole monomer, 0.25 gram of divinylbenzene and 20 milligrams of AIBN and then cured for 24 hours at 70°C under a nitrogen atmosphere.

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 3,700 mg Au/kg of resin from solution.

EXAMPLE 7

1.4 grams of a hydrophilic polyurethane foam was contacted with 0.8 grams of hexamethylene diisocyanate dispersed in 1.5 millilitres of toluene and containing 20 milligrams of triethylamine and then cured for 5 hours at 60°C under nitrogen. The resultant resin was then further reacted with diethylene triamine at 60°C for 12 hours under nitrogen.

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 4,000 mg Au/kg of resin from solution.

EXAMPLE 8

25 grams of a 4800 MW glycerine-based poly(ethylene oxide)-poly(propylene oxide) polyol was slowly reacted with a mixture consisting of 15 grams of the same EO-PO polyol, 10 grams of 1-vinylimidazole and 0.25 grams of AIBN to produce a polymer polyol.

- 25 -

A polyurethane foam was produced as follows:

5 a mixture consisting of 18.7 grams of the polymer polyol containing the polymerised vinylimidazole, 5 grams of a 4800 MW glycerine-based EO-PO polyol, 0.4 grams of water, 0.2 grams of a silane-based surfactant and 0.1 grams of stannous octoate was reacted to produce a polyurethane foam by rapidly stirring this mixture for 10 seconds with 5 grams of toluene diisocyanate (TDI).

10 0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 2,400 mg Au/kg of resin from solution.

15 EXAMPLE 9

20 25 grams of a 4800 MW glycerine-based poly(ethylene oxide)-poly(propylene oxide) polyol was slowly reacted with a mixture consisting of 15 grams of the same EO-PO polyol, 10 grams of [3-(methacryloyl-amino)propyl]trimethylammonium chloride and 0.25 grams of 4,4' azobis(4-cyanopentanoic) acid to produce a polymer polyol.

25 A polyurethane foam was produced as follows:

30 a mixture consisting of 18 grams of the polymer polyol containing the [3-(methacryloylamino)propyl]trimethylammonium chloride polymer, 5 grams of a 5000 MW glycerine-based EO-PO polyol, 0.72 grams of water, 0.2 grams of a silane-based surfactant, 2 grams of methylene chloride, 0.03 grams of stannous octoate and 0.13 grams of a 7:6 mixture of DMEA-DABCO was reacted to form a polyurethane foam by rapidly stirring this mixture for 35 10 seconds with 8.1 grams of TDI.

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 4,200 mg Au/kg of resin from solution.

5

EXAMPLE 10

25 grams of a 4800 MW glycerine-based poly(ethylene oxide)-poly(propylene oxide) polyol was slowly reacted with a mixture consisting of 15 grams of the same EO-PO polyol, 20 grams of vinyl acetate and 0.25 grams of AIBN to produce a polymer polyol.

A polyurethane foam was produced as follows:

15

a mixture consisting of 22.5 grams of the polymer polyol containing the vinylacetate polymer, 5 grams of a 5000 MW glycerine-based EO-PO polyol, 0.72 grams of water, 0.2 grams of a silane-based surfactant, 2 grams of methylene chloride, 0.03 grams of stannous octoate and 0.13 grams of a 7:6 mixture of DMEA-DABCO was reacted to form a polyurethane foam by rapidly stirring this mixture for 10 seconds with 8.1 grams of TDI.

0.5 grams of the above resin was reacted with 0.3 grams of diethylenetriamine in 25 millilitres of toluene at 70°C for 18 hours. The product was washed with toluene and dried under vacuum at 60°C.

0.1 gram of this polymer was then pulsed for 3 hours in 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded 4,700 mg Au/kg of resin from solution.

35 EXAMPLE 11

The polymer loaded with gold cyanide from Example 7 was contacted with 20 millilitres of a 1 molar solution of sodium

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hydroxide at room temperature for 18 hours. The gold cyanide was eluted from the polymer.

EXAMPLE 12

5

The guanidine-based polymer loaded with gold cyanide from Example 3 was contacted with 20 millilitres of a 1 molar solution of sodium hydroxide at room temperature for 18 hours. The gold cyanide was eluted from the polymer.

10

EXAMPLE 13

The resin in Example 7 was contacted at room temperature with a solution containing 160 ppm of free cyanide ions together with the following metal cyanide complexes at a pH of 10.5 for 1 hour and 3 hours to give the sorption results below:

Metal Cyanide	Initial Conc. ppm	Loading, mg metal/kg resin	
		1 hour	3 hours
Au	8.58	3,520	3,500
Ag	2.09	340	240
Zn	2.60	400	800
Ni	2.12	80	180
Co	1.51	20	20
Cu	5.52	200	240
Fe	5.59	0	0

EXAMPLE 14

30

The dimethylamine-based resin in Example 3 was contacted at room temperature with a solution containing 160 ppm of free cyanide ions together with the following metal cyanide

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complexes at a pH of 10.5 for 1 hour, 3 hours and 24 hours to give the sorption results below:

5	Metal Cyanide	Initial Conc. ppm	Loading, mg metal/kg resin		
			1 hour	3 hour	24 hour
	Au	8.57	6,040	5,980	5,860
	Ag	2.35	0	0	984
	Zn	2.00	0	0	200
	Ni	2.32	120	80	140
10	Co	1.59	40	20	120
	Cu	5.58	1,080	960	560
	Fe	5.41	0	0	440

15 EXAMPLE 15

Styryl guanidine monomer was synthesised. 1.5 grams of a polyurethane foam in which 10 % by weight of polybutadiene diol was included as a raw material during its manufacture was
20 interpenetrated with a mixture of 4 grams of this monomer, 0.1 gram of divinylbenzene and 18 milligrams of AIBN and then cured for 24 hours at 70°C under a nitrogen atmosphere.

0.1 gram of this polymer was then pulsed for 3 hours in
25 20 millilitres of a 50 ppm solution of potassium gold cyanide at a pH of 11. The polymer loaded >5,000 mg Au/kg of resin from solution.

CLAIMS:-

1. A gold complex and/or silver complex selective ion exchange resin comprising a polyurethane matrix having an
5 amine functionality.
2. A resin according to claim 1 wherein a second polymer is dispersed or distributed throughout said polyurethane matrix, said second polymer being provided with said amine
10 functionality.
3. An ion exchange resin according to claim 2 wherein said second polymer is a polymer formed from monomers of styrene, acrylonitrile, vinyl chloride, vinylidene chloride, divinyl
15 benzene, butadiene, epichlorohydrin, caprolactone, thiodiglycol, thiodianiline, diallylamine, methylacrylonitrile, hydrazides, dicyclopentadiene, vinyl butyral, succinic anhydride, allyl halides, allyl malonic acid, acryloyl chloride, polyacetal, vinyl alcohol,
20 aminosalicyclic acid, dimethylolpropionic acid, α -methyl styrene, p-methyl styrene, acrylates such as methylmethacrylate, acrylamide, methylacrylamide, acrylic acid, hydroxyethyl acrylate, hydroxypropyl acrylate, glycidyl methacrylate, ethylene dimethacrylate, methylacrylic acid,
25 hydroxyethyl methacrylate, ethylene glycol dimethacrylate, ethyl acrylate, acrylimido salicylic acid, acrylimido diacetic acid, acrylimido malonic acid, acrylimido phthalic acid, acrylimido glycolic acid, N,N'-methylenebisacrylamide, 1-vinylimidazole, vinylpyridine, styrylguanidine complexes,
30 diallyldimethylammonium chloride, styryl imidazoline complexes, or combinations of these monomers or chemical modifications of these monomers.
4. An ion exchange resin according to claim 3 wherein the
35 chemically modified monomers are selected from styrene, divinylbenzene, chloromethylstyrene, acrylonitrile and acrylates, including methylmethacrylate.

- 30 -

5. An ion exchange resin according to claim 2 wherein said second polymer is selected from polystyrene, styrene-divinyl benzene, styrene-acrylonitrile, styrene-acrylonitrile-methylmethacrylate, acrylonitrile-methylmethacrylate, polyacrylonitrile, polyacrylates, acrylic or methacrylic esters, acrylonitrile-unsaturated dicarboxylic acid-styrene, vinylidene chloride-acrylonitrile, epoxy(glycidyl methacrylate)-acrylonitrile, poly p-methylstyrene, polyureas, aniline-phenol-formaldehyde, phenol-formaldehyde, styrene-butadiene, styrene-acrylonitrile-butadiene, acrylonitrile-polyethylene glycol, polyamides, polyacrylamides, polyimidazoles, allylglycidyl ether adducts of diamines, ethylene and propylene carbonate adducts of diamines, polybutadiene-acrylates, polydiallylamine, epoxy adducts, polycaprolactone, caprolactone-acrylates, polydicyclopentadiene, styrene-methacrylonitrile, methacrylonitrile-divinylbenzene, polyvinyl chloride, glycidyl methacrylate-ethylene dimethacrylate, acrylonitrile-methylacrylic acid, polyvinyl alcohol-acrylonitrile, methyl methacrylate-hydroxyethyl acrylate, hydroxyethyl methacrylate-oligo(ethylene glycol)dimethacrylate, hydroxystyrene-methylmethacrylate, polyethyl acrylate-polystyrene, crosslinked butadiene, polystyrene-polyethyleneimine, polystyrene-arsenazo, epoxy-polystyrene, epoxy-diaza crown ethers, polyacetal, cresol sulphonic acid-phenol-formaldehyde, anthraquinone-formaldehyde, acryloyl chloride-iminodiacetic acid, acryloyl chloride-aminosalicylic acid, acryloyl chloride-methyl nitrophenol-triethylamine, methyl nitrophenol-acetic anhydride-acrylic acid, hydroxy acetophenone-substituted benzoic acid-formaldehyde, or combinations thereof.

6. An ion exchange resin according to claim 3 or claim 5 wherein said second polymer and/or the polyurethane matrix has been chemically modified by chlorination, chloromethylation, carboxylation, amination, phosphorylation, thioureation, diazotization, amidoximation, or oximation in one or more steps to attach ligands to said second polymer.

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7. An ion exchange resin according to claim 1 wherein a polyurethane matrix has been provided with unsaturated sites during its manufacture by incorporation of one or more unsaturated hydroxyl-containing compounds or isocyanate-terminated prepolymers containing these compounds.
8. A polyurethane resin according to claim 7 wherein said unsaturated sites are selected from hydroxyethylacrylate, octene diol, hexene 1,2 diol or polybutadiene diol.
9. An ion exchange resin according to claim 7 wherein the isocyanate-terminated prepolymer is produced from TDI or MDI and by reaction with hydroxyl-containing polyols according to claim 7 or claim 8.
10. An ion exchange resin according to claim 7 wherein one or more unsaturated monomers is interpenetrated into a cured polyurethane matrix and polymerised.
11. An ion exchange resin according to claim 10 wherein said monomers are selected from vinylpyridine, 1-vinylimidazole, diallyldimethylammonium chloride, [3-(methacryloylamino)propyl]trimethylammonium chloride, styryl guanidine and/or its complexes, styrylimidazole and/or its complexes.
12. An ion exchange resin according to claim 1 wherein a copolymer polyol is incorporated as a raw material in the manufacture of said polyurethane matrix, said copolymer polyol being produced by the grafting polymerisation of unsaturated monomers onto poly(ethylene oxide) or poly(propylene oxide) or mixed polyethylene oxide/poly(propylene oxide) containing polyols.
13. An ion exchange resin according to claim 12 wherein said monomers are selected from styrene, divinylbenzene, acrylonitrile, acrylates, vinyl acetate, styryl guanidines, styryl imidazoles, vinylpyridine, 1-vinylimidazole and [3-(methacryloylamino)propyl]-trimethylammonium chloride and

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mixtures thereof.

14. An ion exchange resin according to claim 1 wherein a ligand is incorporated into the polyurethane by reacting a di-
5 or higher functionality isocyanate with hydroxyl and/or amide groups present in a polyurethane polymer.

15. An ion exchange resin according to claim 14 in which amine functionality is introduced into the resin by amination
10 of unreacted isocyanate groups.

16. An ion exchange resin according to claim 1 wherein a diisocyanate is reacted with amide groups and/or hydroxyl groups present in a polyurethane polymer and then ligands are
15 reacted with unreacted isocyanate groups.

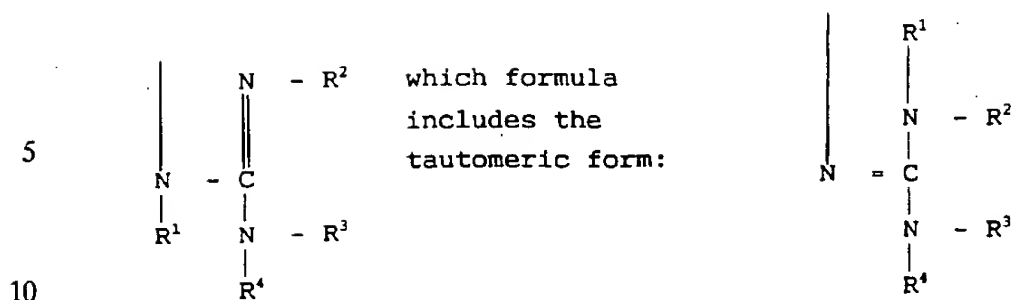
17. An ion exchange resin according to claim 1 wherein said amine functionality is selected from alkyl amines, pyridine, quinoline, benzylamine, dibenzylamine, pyrrolidine,
20 diallylamine, amino diacetate and amino phosphonic acids.

18. An ion exchange resin according to claim 1 wherein said amine functionality is a guanidine functional group or guanidine complex.
25

19. An ion exchange resin according to claim 18 wherein said guanidine functional group is guanidine, 2-ethylhexylguanidine, di-o-tolyl guanidine, di-n-alkyl guanidine, dioctylguanidine, N-(6-aminohexyl)-N'-butyl
30 guanidine complexes, styrylimidazoline complexes.

20. An ion exchange resin according to claim 19 wherein the guanidine functional group or guanidine complex are compounds having the formula:
35

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in which each of R^1 , R^2 , R^3 , and R^4 independently of each other, represent hydrogen, alkyl, alkenyl or aryl (including substituted aryl) with the further possibility that the functional group may be protonated and have a counter ion associated therewith; or

compounds containing the functional group



wherein R_1 through R_5 is selected from the group consisting of H, a resin, or aromatic and aliphatic groups containing from 2-25 carbon atoms.

21. An ion exchange resin according to claim 17 which is then methylated or ethylated.

30

22. An ion exchange resin according to claim 1 wherein an organic extractant is included into said polyurethane matrix.

23. An ion exchange resin according to claim 22 wherein said organic extractant is an amine extractant selected from tributylphosphate, dibutyl butyl phosphate, trioctylamine, tri-(C_8 - C_{10}) alkyl methyl ammonium chloride, guanidine functionality or imidazoline functionality.

40 24. An ion exchange resin according to claim 1 wherein particles selected from metal powders, metal alloy particles,

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inorganic materials, metal oxides or mixtures thereof are added to said resin to modify the density of said resin and/or to assist in recovery of the resin from aqueous solutions or pulps.

5

25. A process for the extraction of gold and/or silver from solutions including the steps of:

- (a) contacting a gold complex and/or silver complex containing solution with a resin as claimed in claim 1;
- (b) separating the resin; and
- (c) recovering the sorbed gold complex by elution of the gold complex from the resin.

10

15 26. A process according to claim 25 wherein said gold and/or silver complex is a cyanide complex.

27. A process according to claim 25 in which the gold-containing solution is part of a pulp or slurry of a Resin-in-

20 Pulp process.